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## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

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<b>(54) Title:</b> ALKALINE PEROXIDE LIQUID DETERGENT COMPOSITION  <b>(57) Abstract</b>  Use of an alkali metal perborate or percarbonate salt as a buffering additive in the manufacture of an alkaline peroxide-containing liquid detergent composition, characterised in that the level of the persalt added, based on peroxide equivalent content, is less than 90 %, preferably less than 75 %, most preferably less than half of the total peroxide equivalent in the composition. Also a method of cleaning laundry comprising the direct application to the laundry or a selected part of the laundry of a composition according to any one of claims 5 to 8, optionally followed by a rubbing action.		

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## ALKALINE PEROXIDE LIQUID DETERGENT COMPOSITION

This invention relates to alkaline peroxide liquid detergent compositions for fabric washing.

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To obtain effective detergency from an alkaline liquid detergent composition across a range of use conditions it needs to be buffered. Borax and sesquicarbonate are frequently incorporated into liquid detergent formulations. Both help to maintain a high wash liquor pH. We have found that each of these materials is incompatible with hydrogen peroxide.

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Sesquicarbonate gives the required buffering but it also gives rise to rapid decomposition of peroxide. Borax gives lower, but still unacceptably high, levels of peroxide decomposition.

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Many publications mention the possibility of addition of a persalt such as perborate or percarbonate to an alkaline detergent liquid. Usually it is suggested as a replacement for hydrogen peroxide which is the preferred form of peroxide. If it were to be used in this way then there would be solid persalt present in the composition. Such a use is described in EP-A-294 904 describing the formation of suspended sodium perborate crystals by recrystallisation. There will be a minor amount of hydrogen peroxide and dissolved persalt

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in equilibrium with the recrystallised perborate held in suspension. The reference teaches that this should be minimised by use of a water miscible organic solvent to reduce the solubility of the perborate in the liquid phase.

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WO 93/13012 discloses general purpose alkaline bleaching or disinfecting compositions comprising less than 1% of optional amine oxide surfactant, 0.5% borax, and 5 or 10% hydrogen peroxide. The pH of the formulations tested is adjusted with sodium hydroxide to the relatively low initial value of 8.5 and the 12 week stability data for the 5% hydrogen peroxide formulation without any surfactant stored at about 30°C shows low loss of

peroxide, but it is clear that the buffering is not adequate because the pH drops. There is no suggestion to use anything other than disodium tetraborate decahydrate (borax) as the buffer.

5 WO 93/01270 discloses an alkaline aqueous liquid washing agent comprising surfactant, hydrogen peroxide and a water soluble borate chosen from borax and sodium borate, the mole ratio of peroxide : borate being greater than 1.5:1 and the composition having an initial pH of less than 8 in all the examples. The invention resides in the ability of the water  
10 soluble borate and other ingredients to give a pH rise to about 9 when the composition is diluted. All formulations contain solvents such as ethanol and propylene glycol. Sodium perborate is not used or suggested.

There is no disclosure or suggestion in the prior art that a minor amount of persalt can be used in solution to buffer a liquid containing hydrogen peroxide in solution.

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According to the present invention there is provided use of an alkali metal perborate or percarbonate salt as a buffering additive in the manufacture of an alkaline peroxide-containing liquid detergent composition, characterised in that the level of the persalt added, based on peroxide equivalent content, is less than 90%, preferably less than 75% and most  
20 preferably less than half of the total peroxide equivalent in the composition.

Preferably the buffering additive is dissolved in the liquid detergent composition as this avoids the problem of suspending a solid component. This is especially advantageous if the composition is isotropic.

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The best combination of buffering and peroxide stability is obtained when the buffering additive is perborate, preferably sodium perborate tetrahydrate or monohydrate.

According to a second aspect of the present invention there is provided an alkaline peroxide

liquid detergent composition comprising surfactant, a peroxygen bleach and a soluble buffer, characterised in that the peroxygen bleach is hydrogen peroxide and the buffer is an inorganic persalt selected from alkali metal or alkaline earth salts of perborate and percarbonate, wherein the available oxygen from the hydrogen peroxide exceeds that from the persalt, preferably by at least 2:1 and most preferably by at least 3:1.

### Surfactants

Compositions of the present invention comprise 5-60% by weight surfactants. Peroxide reacts with many surfactants to give reaction products which cause a lowering of the composition pH. By using the buffers of the present invention a wide range of surfactants, which may be selected from anionic, cationic, nonionic, zwitterionic and amphoteric surfactants and blends thereof, may be used. For example, they may be chosen from any of the classes, sub-classes and specific materials described in "Surface Active Agents" Vol. I, by Schwartz & Perry, Interscience 1949 and "Surface Active Agents" Vol. II by Schwartz, Perry & Berch (Interscience 1958), or in "McCutcheon's Emulsifiers & Detergents" published by the McCutcheon division of Manufacturing Confectioners Company or in "Tensid-Taschenbuch", H. Stache, 2nd Edn., Carl Hanser Verlag, Munchen & Wien, 1981.

Suitable nonionic surfactants include, in particular, the reaction products of compounds having a hydrophobic group and a reactive hydrogen atom, for example aliphatic alcohols, acids, amides or alkyl phenols with alkylene oxides, especially ethylene oxide either alone or with propylene oxide. Specific nonionic detergent compounds are alkyl ( $C_{6-18}$ ) primary or secondary linear or branched alcohols with ethylene oxide, and products made by condensation of ethylene oxide with the reaction products of propylene oxide and ethylenediamine. Other so-called nonionic detergent compounds include long chain tertiary amine oxides, long chain tertiary phosphine oxides and dialkyl sulfoxides.

Also possible is the use of salting out resistant active materials, such as described in EP 328 177, especially the use of alkyl poly glycoside surfactants, such as disclosed in EP 70 074.

Suitable anionic surfactants are usually water-soluble alkali metal salts of organic sulphates and sulphonates having alkyl radicals containing from about 8 to about 22 carbon atoms, the term alkyl being used to include the alkyl portion of higher acyl radicals. Examples of suitable synthetic anionic detergent compounds are sodium and potassium alkyl sulphates, especially those obtained by sulphating higher ( $C_{8-18}$ ) alcohols produced for example from tallow or coconut oil, sodium and potassium alkyl ( $C_{9-20}$ ) benzene sulphonates, particularly sodium linear secondary alkyl ( $C_{10-15}$ ) benzene sulphonates; sodium alkyl glyceryl ether sulphates, especially those ethers of the higher alcohols derived from tallow or coconut oil and synthetic alcohols derived from petroleum; sodium coconut oil fatty monoglyceride sulphates and sulphonates; sodium and potassium salts of sulphuric acid esters of higher ( $C_{8-18}$ ) fatty alcohol-alkylene oxide, particularly ethylene oxide, reaction products; the reaction products of fatty acids such as coconut fatty acids esterified with isethionic acid and neutralised with sodium hydroxide; sodium and potassium salts of fatty acids amides of methyl taurine; alkane monosulphonates such as those derived by reacting alpha olefins ( $C_{8-20}$ ) with sodium bisulphite and those derived from reacting paraffins with  $SO_2$  and  $Cl_2$  and then hydrolysing with a base to produce a random sulphonate; and olefin sulphonates, which term is used to describe the material made by reacting olefins, particularly  $C_{10-20}$  alpha-olefins, with  $SO_3$  and then neutralising and hydrolysing the reaction product. The preferred anionic detergent compounds are sodium ( $C_{11-15}$ ) alkyl benzene sulphonates and derivatives of amino acids, such as oleyl sarcosinates, may also be used.

It is also possible to include an alkali metal soap of a fatty acid, especially a soap of an acid having from 12 to 18 carbon atoms, for example oleic acid, ricinoleic acid, and fatty acids derived from castor oil, alkylsuccinic acid, rapeseed oil, groundnut oil, coconut oil, palmkernel oil or mixtures thereof. The sodium or potassium soaps of these acids can be used.

The total detergent active material may be present at from 0.5% to 60% by weight of the total composition, for example from 1% to 40% and typically from 2% to 20% by weight. However, one preferred class of compositions comprises from 3-12% of detergent active material based on the weight of the total composition. The actual amount of surfactant used will depend on the application, a hard surface cleaner will have a low amount, a fabric pre-treatment composition a rather higher amount and a concentrated detergent a high amount.

### Optional Ingredients

10 Compositions of the invention may be isotropic (unstructured) or structured. Structured liquids of the invention may be internally structured whereby the structure is formed by the detergent active materials in the composition or externally structured. Preferably compositions of the invention are isotropic.

15 Viscosity may be regulated by use of one or more hydrotropes. It is preferred to avoid use of 1, 2 diols.

Compositions of the invention may also comprise materials for adjusting the pH. For lowering the pH it is preferred to use weak acids, especially organic acids, most preferred is the use of  $C_{1-8}$  carboxylic acids, the preferred carboxylic acid is citric acid. The use of these pH lowering agents is especially preferred when the compositions of the invention contain enzymes such as amylases, proteases and lipolases. For raising the pH it is preferred to use sodium hydroxide, preferably pre-sequestered.

25 Apart from the ingredients already mentioned, a number of other optional ingredients may also be present at levels below 5%, for example lather boosters such as alkanolamides, particularly the monoethanolamides derived from palm kernel fatty acids and coconut fatty acids, fabric softeners such as clays, amines and amine oxides, lather depressants, suds regulators, inorganic salts, and, usually present in very minor amounts, opacifiers,

fluorescent agents, and optical brighteners, perfumes, germicides, colorants and dyes, and enzymes and enzymatic stabilising agents.

5 Other additives that may be incorporated are soil release agents such as Carboxymethyl cellulose, also known as anti-redeposition agents; dye transfer inhibiting polymers such as polyvinylpyrrolidone and optical brightening additives (OBAs) such as distyryl biphenyl derivatives.

10 Compositions of the invention preferably comprise from 10-93% by weight of water, more preferably from 15-90%, most preferably from 40-88%.

Compositions of the present invention may comprise one or more bleach precursor agents. A well-known example of such an agent is TAED. Preferably the bleach precursor agent is present in the system in at least partly undissolved form.

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In use the detergent compositions of the invention will be diluted with wash water to form a wash liquor for instance for use in a washing machine. The concentration of liquid detergent composition in the wash liquor is preferably from 0.05 to 10%, more preferred from 0.1 to 3% by weight. The compositions can also be applied neat to a soiled garment as a pre-treatment. The buffering makes them particularly beneficial for such use because they retain alkalinity in storage and use and have a higher detergency against oily stains than an unbuffered or acid liquid. Hard surface cleaners and general purpose cleaners are also used neat; but may be diluted if required.

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## 25 Builders

The present compositions may contain a builder, preferably at a level no more than 50%, more preferably at a level of from 5% to 40% of the total composition.



If present, such builders can consist of inorganic or organic types, organic builders are preferred.

The liquid detergent compositions herein optionally may contain, as a builder, a fatty acid component. Preferably, however, the amount of fatty acid is less than 10% by weight of the composition, more preferably less than 4%. Preferred saturated fatty acids have from 10 to 16, more preferably 12 to 14 carbon atoms. Preferred unsaturated fatty acids are oleic acid and palmitoleic acid.

Examples of organic builders are polyacids such as citric acid, nitrilotriacetic acid, and mixtures of tartrate monosuccinate with tartrate disuccinate. Preferred builders for use herein are citric acid and  $C_{10-16}$  alk(en)yl-substituted succinic acid compounds. An example of this group of compounds is dodecyl succinic acid. Polymeric carboxylate builders such as polyacrylates, polyhydroxy acrylates and polyacrylates/polymaleates copolymers can also be used.

#### Sequestrants

The compositions herein may also contain other components and/or additives at a level preferably less than about 5%. Non-limiting examples of such additives, which can more preferably be used at levels from 0.03% to 2%, include polyaminocarboxylate additives such as ethylenediaminetetracetic acid, diethylenetriamino-pentacetic acid, ethylenediamino disuccinic acid or the water-soluble alkali metals thereof. Other additives useful at these levels include organo-phosphonic acids; particularly preferred are ethylenediamino tetramethylenephosphonic acid, diethylenetriamino pentamethylenephosphonic acid, aminotrimethylenephosphonic acid, and hydroxyethylidene diphosphonic acid. Bleach stabilisers such as dipicolinic acid, sodium stannates and 8-hydroxyquinoline can also be included in these compositions at these levels, preferably at levels from between 0.01 to 1%.

Particularly preferred combinations of sequestrants are disclosed in PCT/GB95/01537 and comprise sodium diethylene triamine penta(methylene phosphonate) such as is sold as Dequest 2066 by Monsanto (and referred to hereinafter as D2066) and 2,2'-dipyridylamine (hereinafter referred to as DPA) and D2066 and 1,2-diaminocyclohexyl tetra (methylene phosphonic acid) and salts thereof (hereinafter referred to as DACH).

The combination of sequestering agents gives a universal sequestering performance on transition metal ions. In general these can be separated into two groups, Group A and Group B.

The Group A sequestering agent preferably comprises one or a mixture of more than one sequestering agents which is effective for stabilising peroxide against decomposition by cobalt II ions under alkaline conditions. They may also be effective for sequestering the other transition metal ions. The Group B sequestering agent comprises one or a mixture of more than one sequestering agent which is effective for stabilising peroxide against iron, copper or manganese under alkaline conditions but substantially ineffective in stabilising peroxide against decomposition by cobalt.

The Group A sequestering agent is preferably selected from compounds having nitrogen donors as ligands, such as triazacycloalkane compounds especially 1,4,7-triazacyclononanes (TACN), or DPA, as well as some phosphonate compounds wherein the molecule has limited flexibility and appropriate spacing of the ligands such as DACH. DACH and/or DPA are particularly preferred. The group B sequestering agent is preferably a non-cyclic alkylene amino poly(methylene phosphonic acid) or other phosphonic acid compound or salt thereof, especially the following agents under the tradename Dequest : such as Dequest 2006 (aminotris(methylene phosphonic acid)) sodium salt; ethylene diamine tetra (methylene phosphonic acid) or the sodium or potassium salt (e.g. Dequest 2046 which is the sodium salt) and diethylenetriaminepenta (methylene phosphonic acid) (Dequest 2060) or 1-hydroxyethane-1, 1-diphosphonic acid sold as Dequest 2010 or analogues with higher

alkylidene groups. D2060 and its sodium salt D2066 are particularly preferred. Other Group B useful sequestering agents are those sold under the tradename Briquest from Albright and Wilson.

- 5 The composition is preferably ethanol-free, more preferably free of all volatile monohydric alcohols (i.e. having flash point about the same as or lower than isopropyl alcohol). The concentrate composition is alkaline. Preferably, the composition will have an initial pH of at least 9, preferably 9 to 11 and most preferably 9.5 to 10. The pH of the composition after 6 weeks storage at 37°C is preferably still greater than 9 and after 12 weeks storage  
10 it is still greater than 8.5.

- The amount of the Group B sequestering agent to be incorporated into the oxidising composition of the invention is at least 0.005% by weight, preferably at least 0.01% by weight. Generally, it will be no greater than 2% by weight, preferably no greater than 1%  
15 by weight and most preferably no greater than 0.5% by weight of the total composition.

- The amount of the Group A sequestering agent to be incorporated into the oxidising composition of the invention is at least 0.005% by weight, preferably at least 0.01% by weight, preferably no greater than 2% by weight or no greater than 1% by weight or, more  
20 particularly from 0.02 to 0.6% by weight.

- Further optional sequestering agents may also be incorporated in the oxidising composition. Where present, such further optional sequestering agents are preferably added in amounts of at least 0.0005% by weight, preferably no greater than 2% by weight, more particularly  
25 in the range of from 0.01% to 1.0%, most preferably in the range from 0.02 to 0.6%, by weight.

The invention will now be described with reference to the following non-limiting examples.

**Examples 1-2 and Comparative Example A**

Test formulations were prepared using 0.3% sodium percarbonate (Example 1) and 0.5% sodium perborate tetrahydrate (Example 2). They were compared against a control without buffer and comparative example A which contained 2% sesquicarbonate. Table 1 shows the results. Sodium percarbonate does not give such effective peroxide retention as the sodium perborate. Nevertheless the percarbonate buffering system could be used either alone or in admixture with perborate for detergents with short shelf-life requirements. The sesquicarbonate gave good buffering but the peroxide loss is unacceptable. Further experiments showed that borax gave buffering which was marginally worse than Examples 1 and 2, but the peroxide loss was much worse.

**Table 1**

Example	% Peroxide loss 37°C			
	1 Week	3 Weeks	4 Weeks	6 Weeks
Control	0	2.91	0.97	9.71
1	1.08	8.6	6.45	9.68
2	1.01	3.03	2.02	5.05
A	34.29	66.67	74.29	92.38
Example	pH 37°C			
	1 Week	3 Weeks	4 Weeks	6 Weeks
Control	9.55	9.35	9.34	8.88
1	9.81	9.7	9.69	9.47
2	9.65	9.51	9.52	9.37
A	9.91	10.00	10.02	9.96

Examples 3 and 4

Chlorine is added to mains water for disinfection. Sometimes the level of chlorine is so high that it can lead to fabric dye damage when clothes are repeatedly washed in it. The use of low levels of peroxide in a liquid detergent formulation should cause a reaction with the chlorine which will reduce chlorine bleaching. Peroxide also provides enhanced bleaching in solution to give reduced damage from dye transfer during the wash. Such a "colour safe" formulation requires the use of a buffer for pH stability on storage if it is to deliver satisfactory removal of fatty soil in the wash.

Colour safe liquid compositions were prepared containing as surfactant a 10:2 ratio of a Primary alcohol ( $C_{13-15}$ ) ethoxylate, ethoxylated with 7 moles of ethylene oxide : linear alkyl ( $C_{10-13}$ ) benzene sulphonic acid; giving a total of 12% actives. The composition also included 2%w/w sodium citrate as a builder, 0.02%w/w Acid Blue 80 dye as colorant and 0.20% Tinopal CBS-X a distyryl biphenyl derivative ex Ciba Geigy, as an optical brightening agent. All the compositions had a sequestrant system. Control 1 and Example 4 were sequestered with just 0.1% Dequest 2066 and Control 2, Examples 3A and 3B were sequestered with 0.1% Dequest 2066 and 0.03% DPA. The initial pH of the liquids was adjusted to 10 using 50%w/w sodium hydroxide (containing 0.5%w/w Dequest 2066). Peroxide was added either as 60% w/w  $H_2O_2$  solution alone (in the controls) or with 0.5% w/w sodium perborate tetrahydrate as a buffer, to give 1% w/w total hydrogen peroxide equivalents in the controls and the examples. The order of addition of the components was perborate, then peroxide solution, then sodium hydroxide. The composition of the examples was as follows:

Control 1	- 1% $H_2O_2$ (no buffer)
Control 2	- 1% $H_2O_2$ (no buffer)
Example 3A and 3B	- 0.85% $H_2O_2$ + 0.5%w/w sodium perborate buffer
Example 4	- 0.85% $H_2O_2$ + 0.5%w/w sodium perborate buffer

Examples 3A and 3B were prepared as identical duplicates to check the reproducibility of the buffered system. Reproducible stability is a key requirement for a commercial system. Many of the prior art systems are capable of giving good stability on a one off basis but the effect is not reproducible.

The formulations were stored at 25 and 37°C and the pH and available oxygen measured periodically. The results are given in Table 2.

Table 2

Example	pH				
	Initial pH	2 Week	4 Week	6 Week	
		37°C	37°C	25°C	37°C
Control 1	10.01	8.98	8.63	9.71	8.46
Control 2	10.01	8.65	8.04	8.86	7.71
3A	10.02	9.72	9.6	9.74	9.46
3B	10.01	9.81	9.61	9.78	9.48
4	10.01	9.69	9.53	9.78	9.31
Example	Initial % Peroxide Added	% Peroxide loss			
		2 Week	4 Week	6 Week	
		37°C	37°C	25°C	37°C
Control 1	1.05	2.86	5.71	0.00	5.71
Control 2	1.01	1.98	2.97	0.99	2.97
3A	0.99	5.05	5.05	1.01	6.06
3B	0.99	3.03	3.03	1.01	6.06
4	1.00	4.00	3.00	2.00	7.00

Buffering is significantly improved in duplicate examples 3A and 3B containing 0.5% w/w

sodium perborate tetrahydrate in solution as a buffer. All examples show similar peroxide stability after 4 weeks storage at 37°C. It is known that peroxide is inherently more stable when the pH is lower. The stability of the two examples containing sodium perborate tetrahydrate is reproducible especially for longer test periods. The beneficial effect of using the soluble persalt as a buffer is obtained for both sequestrant systems.

The wide utility of the invention is further illustrated by the following compositions which may be formulated using the buffering system which forms the subject of the invention:

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**Example 5. Kitchen Spray Cleaner**

	%
Deionised Water	To 100
15 Hydrogen Peroxide (as 100%)	3.00
PBS4	0.50
Dequest 2066	0.25
DPA	0.02
Sodium Hydroxide	To pH 9.5
20 Synperonic A7	2.50
*Proglyde DMM	3.00

\* Dipropylene glycol dimethyl ether

**Example 6. Hard Surface Cleaner**

		%
	Deionised Water	To 100
5	Hydrogen Peroxide (as 100%)	4.30
	PBS4	1.00
	Synperonic A7	3.00
	DPA	0.03
	Dequest 2066	0.25
10	Sodium Hydroxide	To pH 9.5

**Example 7 General Purpose Cleaner**

		%
15	Deionised Water	To 100
	Hydrogen Peroxide (as 100%)	3.70
	Citric Acid	3.00
	PBS4	3.00
20	Dequest 2066	0.25
	DPA	0.02
	Sodium Hydroxide	To pH 9.50
	Synperonic A7	7.00



**Example 8     Dual Compartment Fabric Washing Liquid**

		%
5	Deionised Water	To 100
	Secondary Alkane Sulphonate	8.00
	Synperonic A7	2.00
	Citric Acid	3.00
	Dequest 2066	0.50
10	DPA	0.03
	Silicone Oil	0.10
	Hydrogen Peroxide (as 100%)	3.50
	Sodium Hydroxide	To pH 9.50
	PBS4	3.00

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**CLAIMS**

1. Use of an alkali metal perborate or percarbonate salt as a buffering additive in the  
5 manufacture of an alkaline peroxide-containing liquid detergent composition, characterised in that the level of the persalt added, based on peroxide equivalent content, is less than 90%, preferably less than 75%, most preferably less than half of the total peroxide equivalent in the composition.
- 10 2. Use as claimed in claim 1 wherein the buffering additive is substantially fully dissolved in the liquid detergent composition.
3. Use as claimed in claim 1 wherein the buffering additive is a perborate salt.
- 15 4. Use as claimed in claim 3 wherein the buffering additive is sodium perborate tetrahydrate or monohydrate.
5. An alkaline peroxide liquid detergent composition comprising surfactant, a peroxygen bleach and a soluble buffer, characterised in that the peroxygen bleach  
20 is hydrogen peroxide and the buffer is an inorganic persalt selected from alkali salts of perborate and percarbonate, wherein the available oxygen from the hydrogen peroxide exceeds that from the persalt preferably by at least 2:1, most preferably by at least 3:1.
- 25 6. A composition according to claim 5 which further comprises a sequestrant system, preferably a combination of two sequestrants, one being a group A sequestrant and the other a group B sequestrant as defined herein.
7. A composition according to claim 5 or 6 in which the inorganic persalt is sodium

perborate tetrahydrate or sodium perborate monohydrate.

8. An activated peroxygen bleaching system comprising a dispensing container with two compartments one of which contains a bleach activator and the other of which contains a composition as claimed in claims 1 to 7.
9. A method of cleaning laundry comprising the direct application to the laundry or a selected part of the laundry of a composition according to any one of claims 5 to 8, optionally followed by a rubbing action.
10. A method of cleaning laundry according to claim 9 in which the direct application is followed by washing the laundry in an automatic washing machine with the additional use of a conventional laundry detergent, optionally containing a bleach activator such as tetraacetyl ethylenediamine.



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(21) International Application Number: <b>PCT/GB97/01450</b> (22) International Filing Date: <b>28 May 1997 (28.05.97)</b> (30) Priority Data: <b>9611062.2</b> <b>28 May 1996 (28.05.96)</b> <b>GB</b> (71) Applicant (for all designated States except US): <b>WARWICK INTERNATIONAL GROUP LTD. [GB/GB]; Mostyn, Holywell, Clwydd CH8 9HE (GB).</b> (72) Inventors; and (75) Inventors/Applicants (for US only): <b>TOMPSETT, Stephen, James [GB/GB]; 75 Main Street, Burley-in-Wharfedale, West Yorkshire LS29 7BU (GB). TURNER, Neil, A. [GB/GB]; 10 Hillsdown Way, Great Sutton, South Wirral L66 2HU (GB).</b> (74) Agent: <b>GILL JENNINGS &amp; EVERY; Broadgate House, 7 Eldon Street, London EC2M 7LH (GB).</b>			(81) Designated States: <b>AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, GH, HU, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ARIPO patent (GH, KE, LS, MW, SD, SZ, UG), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).</b>  <b>Published</b> <i>With international search report.</i> <i>Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>  (88) Date of publication of the international search report: <b>19 February 1998 (19.02.98)</b>
(54) Title: <b>ALKALINE PEROXIDE LIQUID DETERGENT COMPOSITION</b>			
(57) Abstract <p>Use of an alkali metal perborate or percarbonate salt as a buffering additive in the manufacture of an alkaline peroxide-containing liquid detergent composition, characterised in that the level of the persalt added, based on peroxide equivalent content, is less than 90 %, preferably less than 75 %, most preferably less than half of the total peroxide equivalent in the composition. Also a method of cleaning laundry comprising the direct application to the laundry or a selected part of the laundry of a composition according to any one of claims 5 to 8, optionally followed by a rubbing action.</p>			

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# INTERNATIONAL SEARCH REPORT

International Application No.  
PCT/GB 97/01450

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 C11D3/39

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C11D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 93 13012 A (SOLVAY INTEROX LTD ; JEYES LTD (GB)) 8 July 1993 cited in the application see claim 1	1-5,7
A	WO 93 01270 A (HENKEL KGAA) 21 January 1993 cited in the application see page 5, line 23 - line 29 see page 6, line 29 - page 7, line 5 see page 2, line 27 - line 31	1-7,9,10
A	WO 93 14183 A (PROCTER & GAMBLE) 22 July 1993 see claims 1,4	1-7,9,10

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☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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Date of the actual completion of the international search

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PCT/GB 97/01450

## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 96 01310 A (WARWICK INT GROUP ;CROUD VINCENT BRIAN (GB); TOMPSETT STEPHEN JAME) 18 January 1996 see page 6, line 26 - line 37 see page 7, line 11 - line 35 see page 11, line 31 - line 32 ---	1-7,9,10
A	WO 91 09103 A (PROCTER & GAMBLE) 27 June 1991 see claims 1-13 see page 15, line 1 - page 17, line 3 ---	1-5,7,9,10
A	US 4 166 794 A (GREY SEYMOUR) 4 September 1979 see column 3, line 56 - line 67 see column 4, line 8 - line 15 see claims 1,13 ---	1-5,7,9,10
A	EP 0 346 835 A (BASF CORP) 20 December 1989 see claims 1,3 see column 4, line 39 - line 40 ---	1-5,7
A	WO 95 16023 A (UNILEVER PLC ;UNILEVER NV (NL); SMITH GILLIAN (GB); SMITH ROYSTON) 15 June 1995 see claim 1 ---	8
A	EP 0 414 462 A (UNILEVER PLC ;UNILEVER NV (NL)) 27 February 1991 see claim 1 see figures 1-3 ---	8
A	GB 2 187 748 A (UNILEVER PLC) 16 September 1987 see claim 4 see figures 1,2 -----	8



# INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No.

PCT/GB 90/01450

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 9313012 A	08-07-93	AT 141241 T	15-08-96
		AU 3167693 A	28-07-93
		CA 2126202 A	08-07-93
		DE 69212842 D	19-09-96
		EP 0617697 A	05-10-94
		FI 942978 A	21-06-94
		JP 7502482 T	16-03-95
		NO 942352 A	20-06-94
		ZA 9209922 A	24-06-93
		BR 9206972 A	05-12-95
		EP 0549348 A	30-06-93
		JP 5271193 A	19-10-93
		US 5639884 A	17-06-97
		US 5587385 A	24-12-96
WO 9301270 A	21-01-93	DE 4123142 A	14-01-93
WO 9314183 A	22-07-93	US 5244593 A	14-09-93
		AU 3440393 A	03-08-93
		BR 9305722 A	31-12-96
		CA 2127438 A	22-07-93
		CN 1075161 A	11-08-93
		EP 0620843 A	26-10-94
		MX 9300122 A	30-06-94
WO 9601310 A	18-01-96	AU 2801195 A	25-01-96
		AU 2801295 A	25-01-96
		AU 2801395 A	25-01-96
		EP 0769046 A	23-04-97
		EP 0769047 A	23-04-97
		WO 9601309 A	18-01-96
		WO 9601311 A	18-01-96
WO 9109103 A	27-06-91	AU 7078491 A	18-07-91
		CA 2069937 A	20-06-91
		EP 0506874 A	07-10-92
		MX 172446 B	16-12-93
US 4166794 A	04-09-79	BE 876537 A	17-09-79
		CA 1116814 A	26-01-82

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/GB 97/01450

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 4166794 A		CH 656042 A	13-06-86
		DE 2920453 A	06-12-79
		DK 217279 A	26-11-79
		FR 2426733 A	21-12-79
		GB 2022641 A,B	19-12-79
		NL 7904143 A	27-11-79
		SE 445564 B	30-06-86
		SE 7904249 A	26-11-79
		ZA 7902316 A	31-12-80
EP 0346835 A	20-12-89	AT 115179 T	15-12-94
		AU 611808 B	20-06-91
		AU 3630789 A	21-12-89
		CA 1327503 A	08-03-94
		DE 68919755 D	19-01-95
		DE 68919755 T	27-04-95
		JP 2034698 A	05-02-90
		US 5522580 A	04-06-96
		US 5348556 A	20-09-94
		US 5252243 A	12-10-93
		US 5389278 A	14-02-95
WO 9516023 A	15-06-95	AU 1240695 A	27-06-95
		BR 9408256 A	10-12-96
		CN 1141647 A	29-01-97
		EP 0733097 A	25-09-96
		JP 9506130 T	17-06-97
EP 0414462 A	27-02-91	AU 628627 B	17-09-92
		AU 6115990 A	28-02-91
		AU 625911 B	16-07-92
		AU 6116290 A	28-02-91
		CA 2023613 A,C	24-02-91
		CA 2023614 A,C	24-02-91
		DE 69024561 D	15-02-96
		DE 69024561 T	15-05-96
		DE 69025012 D	07-03-96
		DE 69025012 T	20-06-96
		EP 0414463 A	27-02-91
		ES 2082829 T	01-04-96

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/GB 97/01450

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 0414462 A		ES 2081937 T	16-03-96
		JP 3119174 A	21-05-91
		JP 1855859 C	07-07-94
		JP 3119175 A	21-05-91
		TR 24867 A	01-07-92
		US 5160654 A	03-11-92
		US 5132036 A	21-07-92
<hr/>			
GB 2187748 A	16-09-87	NONE	
<hr/>			

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